

## ENDOR Characterization of Free Radicals in Coals at Temperatures Upto 200°C

Naresh Dalal and Jeffrey P. DeLooze, Chemistry Department  
West Virginia University, Morgantown, WV 26506-6045

### Summary

The lack of information about the chemical structure of coal-based radicals has been a major obstacle in the understanding of the structural-chemical reactivity relationship. Our past research has indicated that the electron nuclear double resonance (ENDOR) technique has the potential of providing the most accurate structural information on the coal-based radicals. Unfortunately, the sensitivity of the best available ENDOR instrumentation was too low for liquefaction studies. We have developed an ENDOR probe which yields an increase in the sensitivity of the technique that enables us to investigate the structural-chemical reactivity patterns of coal-based free radicals under mild conditions suitable for liquefaction. We have used this technique to examine chemically characterized Illinois #6 coal at temperatures up to 200°C. Analysis of the resulting ENDOR signals identified at least three different types of protons. Analyses were also performed on the temperature dependence of the ENDOR signal intensity. Efforts are currently being made to enhance the measurement methodology's sensitivity above 200°C.

### Introduction

It is well established that free radicals must play a dominant role in coal liquefaction [1]. Thus, a detailed understanding of the reaction mechanism(s) of the free radicals in coal is thought to be essential for the further improvement in the efficiency of coal liquefaction. However, a lack of knowledge concerning the chemical structure(s) of these same coal-based radicals has been a major hindrance in the development of the possible reaction mechanism(s) and, hence, an impediment to the improvement of liquefaction technology. The difficulty in this aspect has been that the structure(s) of the radicals is (are) complex and, hence, standard methods of radical structure determination, such as ESR, are not adequate. Following earlier leads [2-4], it was felt that the high resolution possible with the electron nuclear double resonance (ENDOR) technique would enable us to provide the much needed structural information on the radicals.

Commercially available ENDOR instrumentation does not provide the sensitivity for the required measurements at temperatures of interest to coal liquefaction scientists. Thus, our first task was the development of a new probe that would enable us to make measurements at 200°C and higher. We have developed such a probe, as described elsewhere [5] and the results obtained with it in the studies of Illinois #6 coal are summarized below. Illinois #6 was chosen because it has been accepted by many researchers as a model coal for liquefaction studies. Thus, it is possible to obtain large amounts of uniformly processed coal along with a detailed analysis of the chemical constituents of each sample.

### Experimental Results

The ENDOR measurements were made with a Bruker ER-200-D ENDOR spectrometer, using an ENDOR probe designed in our laboratory, as described in our earlier report [4]. The ENDOR spectral lineshape was found to be quite sensitive to the instrumental parameters as well as sample preparation. A most important factor was the removal of oxygen from the sample via evacuation: the lower

the overall pressure in the sample tube, the stronger became the ENDOR signals, especially those corresponding to the larger couplings. In order to find the experimental parameters which would lead to the optimum signal-to-noise ratio, we carried out systematic ENDOR measurements on the Illinois #6 coal, by varying the microwave power, radio frequency (rf)-power, and sample temperature.

Figure 1 is a typical plot of the ENDOR spectrum of protons in an Arkwright, West Virginia, coal as reported earlier [4] with the original, non-optimized probe under the previously stated operating parameters. The spectrum shows quite high baseline noise and a poor signal-to-noise ratio.

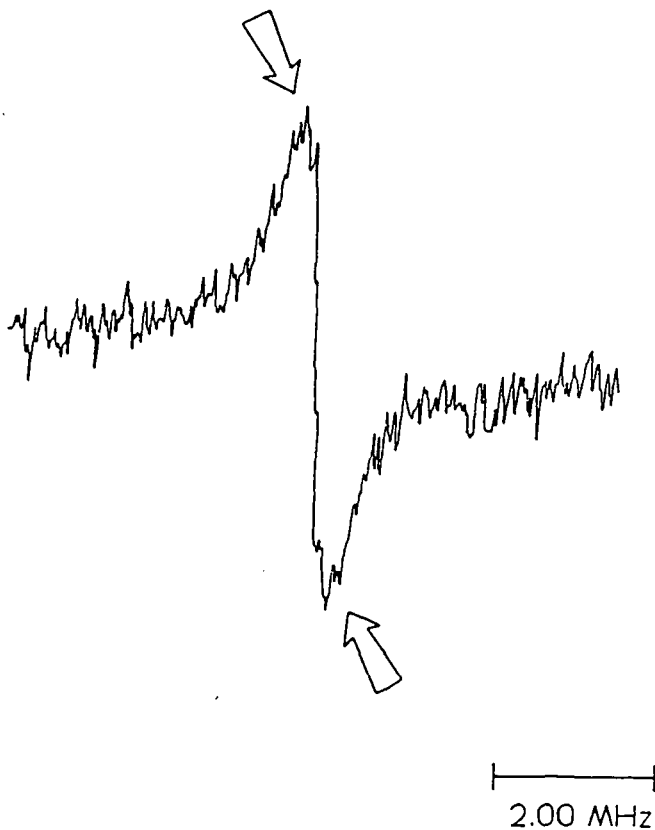


Figure 1: ENDOR spectrum of Arkwright, West Virginia coal sample  
Arrows indicate the sidebands separated by approximately 750 kHz

Figure 2 shows a typical ENDOR spectrum of the Illinois #6 coal, obtained with the new probe; the greatly reduced noise level and, hence, the much higher signal-to-noise ratio is readily apparent. The improvement in the signal-to-noise ratio was found to be at least a factor of 200. This improvement in signal-to-noise also made it possible to obtain still higher spectral resolution via second harmonic detection, as demonstrated by the lower plot in figure 2.

### Comparison of First and Second Derivative ENDOR Spectra

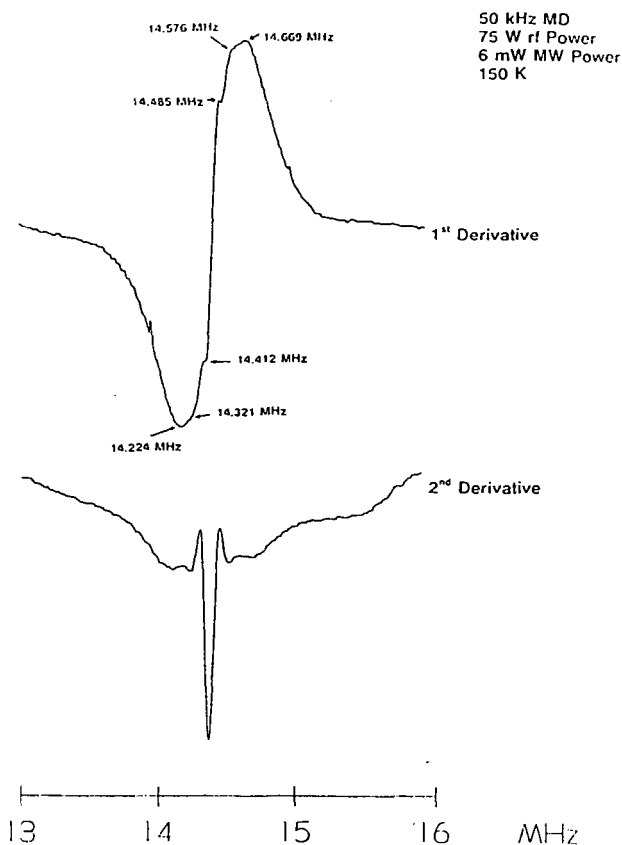


Figure 2: ENDOR spectra of Illinois #6 coal (a) first derivative and (b) second derivative. The higher resolution of the second-derivative presentation (as compared to the first-derivative presentation) can be noted from a comparison of (a) and (b).

Figure 3 is an expanded scale view of the optimized spectra in Figure 2. Note that the apparent discrepancies in the measured ENDOR frequencies is due to the re-tuning of the cavity for optimum response.

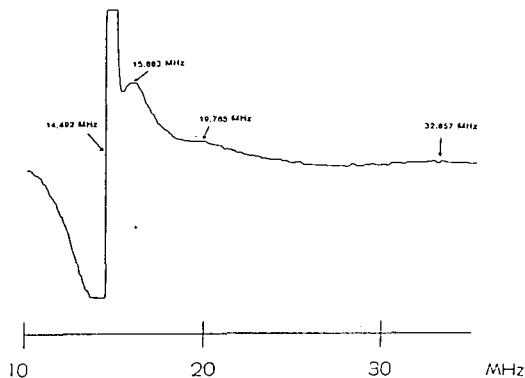


Figure 3: A wide-scan, optimized ENDOR spectrum of Illinois #6 coal at 150K.

Figure 4 shows typical ENDOR spectra of Illinois #6 as a function of temperature. It can be clearly seen that the new probe allows not only for a significant improvement in the room temperature signal, but also provides spectra at previously unheard of temperatures higher than that ever achieved before.

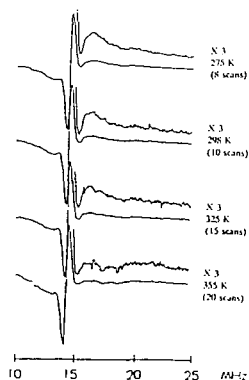


Figure 4: Temperature dependence of the ENDOR spectra of Illinois #6 coal.

Figure 5 shows a plot of the intensity of the ENDOR response as a function of temperature. It is clearly seen that the ENDOR intensity drops as a near-quadratic power function above room temperature to the point that the signals become undetectable above  $\approx 425$  K ( $\approx 150^\circ\text{C}$ ).

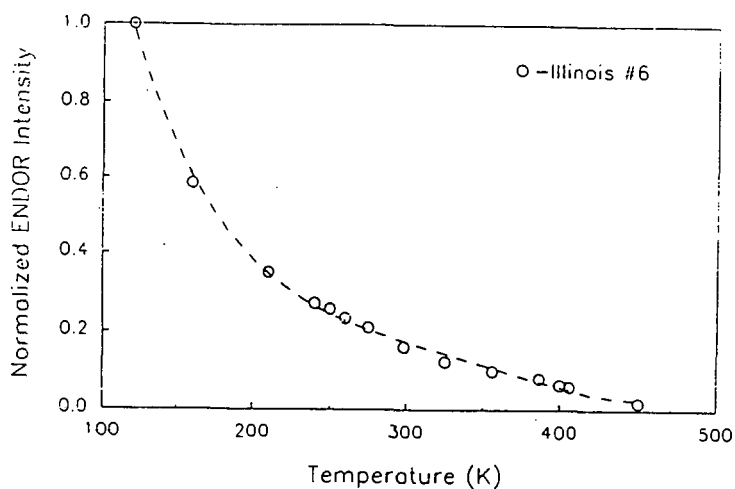


Figure 5: ENDOR signal intensity (optimized) versus temperature for Illinois #6 coal. Signal intensity normalized to  $I_{\text{ENDOR } 120} = 1$ .

### Analysis Procedure

The measured ENDOR frequencies,  $\nu_E$ , were analyzed in terms of the corresponding hyperfine coupling,  $\Delta_H$ , via the following effective spin Hamiltonian [6, 7]:

$$\mathcal{H} = \langle S \rangle \Delta_H \cdot \hat{I} \cdot g_n \beta_n \hat{H} \cdot \hat{I}, \quad (1)$$

where  $\langle S \rangle$  is the effective electron spin;  $\hat{I}$ , the electron spin;  $\hat{H}$ , the applied magnetic field; and  $g_n \beta_n$ , the magnetic moment of the nucleus under consideration, in this case, protons. The general solution of equation (1) will give the energy levels as a function of the applied magnetic field  $\hat{H}$  and the properties of the hyperfine coupling tensor,  $\Delta_H$ . The ENDOR transitions are then given by the differences in the energy levels, with the selection rules  $\Delta m_s = 0$ ,  $\Delta m_I = 1$ , where  $m_s$  and  $m_I$  are the electronic and nuclear spin quantum numbers. In the high-field approximation, i.e., when  $\hat{H} \gg \Delta_H$  (in Gauss), and along the principal directions, the ENDOR transition frequencies,  $\nu_E$ , are related to  $\Delta_H$  and  $\hat{H}$  via:

$$\nu_E = \Delta_H / 2 + g_n \beta_n H \quad (2)$$

For the spectrum shown in figure 3,  $g_n \beta_n H$  was equal to 14.492 MHz, and thus equation (2) provides a direct method of calculating hyperfine couplings from the measured ENDOR frequencies. The hyperfine couplings calculated via equation (2) are listed below in Table 1.

Table 1: Proton ENDOR transition frequencies,  $\nu_E$ , and hyperfine couplings,  $\Delta_H$ , for the free radicals in Illinois #6 coal.

| Proton # | $\nu_E$ / MHz | $\Delta_H$ / MHz | Assignment    |
|----------|---------------|------------------|---------------|
| 1        | 14.448 (two)  | 0.0              | coal matrix   |
| 2        | 15.448        | 2.87             | meta- para-   |
| 3        | 19.765        | 10.63            | ortho-, para- |

It is clear that the ENDOR measurements show that there are essentially three types of protons in the structure of the free radicals in Illinois #6 coal. The majority of the protons, labeled #1 in the table (ref. figure 3), exhibit no measurable isotropic hyperfine coupling with the unpaired electron. These protons are assigned to the coal matrix, although some of these might belong to the radical itself but located at positions of negligible spin density. The second set of protons, labeled #2, exhibits a coupling of about 3 MHz. The third set of protons (labeled #3) exhibits the largest hyperfine coupling ( $\approx 10.6$  MHz).

The above results indicate that the free radicals imbedded in the matrix of the Illinois #6 coal are essentially highly delocalized aromatic structures: protons of type #3 being located at the positions of high spin density, i.e. ortho-to the free electron center. Protons of type #2 might be located at either the meta - or para - positions.

### Theoretical Model

While exact details of the model explaining the rapid decrease in the ENDOR intensity upon heating the Illinois #6 coal have not yet been worked out, it is well established [6] that the ENDOR response is determined by an effective electron-nuclear spin-lattice relaxation time ( $T_{1e}$ ). In general, one then sees that the temperature dependence of the ENDOR signals simply reflects the decrease in  $T_{1e}$ . For simple model compounds,  $T_{1e}$  is a sensitive function of the molecular motion of the radical, given by the autocorrelation function,  $J(\omega_L)$ , as:

$$(T_{1e})^{-1} \approx B_1 J(\omega_L), \text{ where} \quad (3)$$

$$J(\omega_L) = 2 / \tau (1 + \omega_L^2 \tau^2) \quad (4)$$

$$\tau = \tau_0 \exp (E / k_B T) \quad (5)$$

Where  $\tau$  is the correlation time for the relevant molecular motion,  $\tau_0$ , the pre-exponential factor, and  $E$  the activation energy. From these relationships, it is seen that  $T_{1e}$  will decrease rapidly with increase in temperature when  $\omega_L^2 \tau^2 < 1$  (i.e., fast motion limit).

We are now carrying out a detailed analysis of temperature dependence of the ENDOR intensity as shown in figure 4 as assuming different values for  $\tau_0$  and  $E$ . A satisfactory set of these parameters fitting the data in Figure 4 will provide us with further insight into the chemical structure and, more importantly, the relevant molecular motions in the radical entities in the Illinois #6 coal, and likely also in other coals.

### References Cited:

- [1] See for example, H.L. Retcofsky, *Coal Science* **1**, 43 (1982).
- [2] I. Miyagawa and C. Alexander, *Nature* **278**, (1979).
- [3] S. Schlick, P.A. Narayana, and L. Kevan, *J. Am. Chem. Soc.* **100**, 3322 (1978).
- [4] H.L. Retcofsky, M.R. Hough, M.M. Maguire, and R.B. Clarkson, *Appl. Spectrosc.* **36**, 187 (1982).
- [5] N.S. Dalal and J.P. DeLooze, paper presented at the Fifth Annual Technical Meeting of the consortium for fossil Fuel Liquefaction Science, Lexington, Kentucky, August 14, 1991.
- [6] *Electron Spin Double Resonance*, L. Kevan and L.D. Kispert, Wiley Interscience, New York, 1976.
- [7] N.S. Dalal, *Advances in Magnetic Resonance* **10**, 119-218 (1982).